FY2013 LDRD Annual Report

Innovations and Progress

Laboratory Directed
Research and Development
Program Activities

Office of the Director
September 2013

U.S. DEPARTMENT OF
ENERGY

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ABOUT AMES LABORATORY

Ames is a U.S. Department of Energy Laboratory managed by Iowa State University under contract DE-AC02-07CH11358.

The Laboratory's main administration facilities are at 311 TASF on the campus of Iowa State University.

For more information about Ames Lab and its pioneering science and technology programs, see www.ameslab.gov.

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I am pleased to submit the Ames Laboratory's Annual Report on its Laboratory Directed Research and Development (LDRD) activities for fiscal year 2013. Our LDRD Program was inaugurated this year, which also required all projects to be mid-year starts. The LDRD funds enable creative and innovative R&D projects at Ames Laboratory (AMES) that directly support our mission. Selection of projects is the responsibility of the Laboratory Director, with each project identified as strategic in nature and reflects scientific quality, innovativeness, and value to mission-related initiatives.

LDRD is an invaluable resource that permits us to anticipate, and thus be prepared to contribute to, the future science and technology needs of the Department of Energy (DOE) and the nation. The LDRD program objectives are to stimulate innovation and creativity, and to enhance the research activities to keep the Ames Laboratory at the forefront of science and technology. LDRD funding will continuously renew the Laboratory's scientific and technological vitality, and enable AMES to respond to rapidly emerging R&D opportunities of clear potential benefit to DOE's mission. The program enhances AMES' ability to attract and retain the high-caliber scientists and engineers essential to pursue the mission of DOE and the needs of the nation. The LDRD program helps insure that AMES will continue providing scientific and technical leadership in its mission areas.

I can attest that in managing the AMES' LDRD Program, we have adhered without exception to the requirements of DOE Order 413.2b and associated guidelines. Our program management continually strives to be more efficient. In addition to meeting all reporting requirements during FY2013, our LDRD Program Office continues to implement improvements that better serve all LDRD stakeholders, from our researchers, managers, budget office, to our DOE Site Office colleagues.

The individual project reports that follow demonstrate the AMES' researchers have pursued projects at the forefront of their respective fields and have contributed significantly to the advancement of our major initiatives. Evidence of the strength of the program is found from the contributions to significant aspects of the laboratory's Strategic Plan, with future evidence anticipated through follow-on sponsorship and technology transfer.

Tom Lograsso
Interim Laboratory Director

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Acknowledgements

AMES' LDRD Program Office comprises the Chief Research Officer, Dr. Duane D. Johnson, Associate Laboratory Director for Sponsored Research, Deb Covey, and LDRD Program Administrative Specialist, Tessa Lemons. The program reports to the Laboratory Director, Dr. Tom Lograsso (interim), through the Chief Research Officer. The LDRD program's management is grateful for the critical support received throughout the year – from the division's business offices and lab budget office. Special appreciation is due to the many experts who proposed and perform the research and provide the project reports; to the technical and administrative management of AMES' programs and divisions in which the R&D is pursued; to those experts throughout the DOE complex who provide anonymous peer review for LDRD proposals; and to the leaders in the laboratory's strategic initiative areas, whose vision and understanding of the nation's technological needs guide and refine the content of AMES' LDRD portfolio.

Research Reports – by Component

Within a given LDRD Components (Lab Strategic Initiatives, Novel Projects, or Exceptional Opportunities), the projects are list by [LDRD Number], (Strategic/Mission Area) and TITLE.

Novel Projects

Strategic Initiatives

– Materials Discovery, Design, and Development (MADDD)

– Greener Advances in Catalysis for Energy (GrACE)

– Solid-State NMR Sciences (PRIMROSE)

n/a in 2013

Exceptional Opportunities

n/a in 2013

LDRD Objectives

The objectives of AMES' LDRD portfolio are to enhance the Laboratory's ability to achieve its mission by enabling selected critical projects for which no other source of funds is available. LDRD funds will be used: (1) to foster innovation and creativity from the scientific and technical staff by supporting their pursuit of novel, forefront science and technology research ideas, new concepts, and high-risk/high-reward research and development projects; (2) to develop, recruit, and retain the researchers needed to maintain and enhance the scientific, engineering, and technical vitality and capabilities of the Laboratory; (3) to exploit the technical potential of the Laboratory for the benefit of the nation; and (4) to enable the Laboratory's R&D planning by supporting its mission and strategic plans, as described in its Strategic and Lab Plans.

LDRD Components

The program provides support for *Initiatives*, *Novel Projects, and Exceptional Opportunities*.

Strategic Initiatives are employee-initiated proposals that address at least one of the strategic goals or an area of potential growth within AMES' Strategic Initiatives.

The FY2013 **Strategic Initiatives** are as follows:

- Materials Discovery, Design, and Development (MaDDD)
- Greener Advances in Catalysis and Energy (GrACE)
- Primary Research Initiative on Magnetic Resonance of Solid-state for Energy (PRIMROSE)

Novel Projects are a balance of basic, applied, single-investigator, and multidisciplinary projects in new areas or directions, not necessarily in direct support of our initiatives.

Exceptional Opportunities is an integral part of the pursuit of capabilities in a strategic area that enhances human and physical resources to support that area. This component consists of projects that do not fit neatly into the other two or that can arise outside the normal fiscal-year schedule, e.g., strategic hires, collaborations with external institutions where a superior expertise resides, or projects offering exceptional R&D opportunities for AMES. The laboratory director retains the option to identify and support these exceptional types of LDRD projects.

LDRD projects are pursued in forefront areas of basic and applied science and technology that support the DOE mission, enrich Laboratory capabilities, generally advance the knowledge and technology base, and have the potential to generate follow-on funding from DOE offices and programs. Individual LDRD projects will be relatively small and generally fall into one or more of the following categories.

1. Advanced study of hypotheses, concepts, or innovative approaches to scientific, technical, or computational problems.

2. Experiments, theoretical studies, simulations, and analyses directed toward "proof of principle" or early determination of the utility of new scientific ideas, technical concepts and devices, or research tools.

3. Concept creation and preliminary technical analyses of advanced, novel experimental facilities/devices or of facilities for computational science.

LDRD Updates

DOE approved the Ames Laboratory's FY2013 LDRD Plan and expenditures, **not to exceed $900K**. A list of projects begun thus far in FY2013, by project number and title is provided below.

Approved LDRD Plan components:
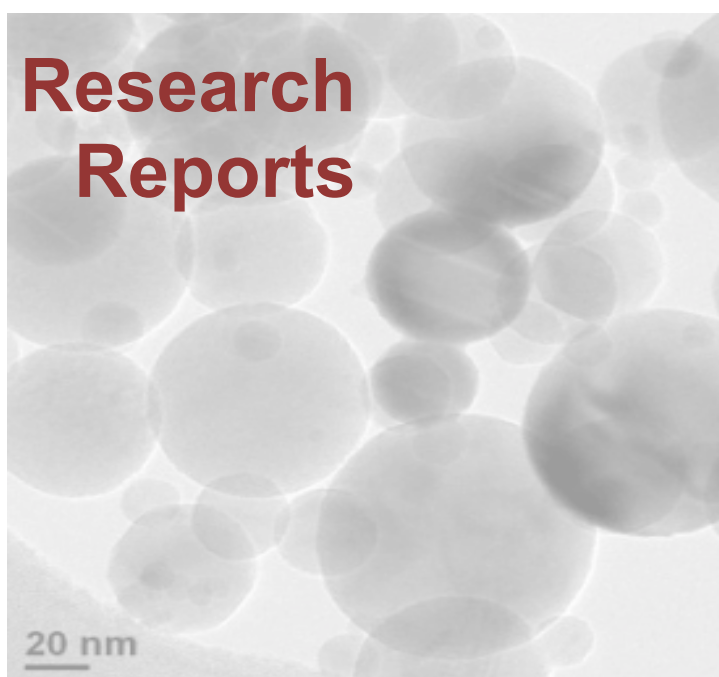*1. Novel Projects*
2. Strategic Initiatives
 – Materials Discovery, Design, and Development (MADDD)
 – Greener Advances in Catalysis for Energy (GrACE)
 – Solid-State NMR Sciences (PRIMROSE)
3. Exceptional Opportunities

Funding Summary ($ in thousands) for Projects Active in FY2013

DOE approved the Ames Laboratory's FY2013 LDRD Plan and expenditures, not to exceed $900K. A list of projects begun thus far in FY2013, by project number and title is provided below.

Proposal No.	2012	2013	2014	2015	Total
Novel Projects					
2013-GOR-1218	0	$89			$89
2013-WAN-0113	0	$49			$49
Strategic Initiatives					
2013-JON-0114	0	$63			$63
2013-AKI-0310	0	$68			$68
2013-FAN-0313	0	$102			$102
2013-HUA-0413	0	$102			$102
Exceptional Opportunities					
	0	0			0
	0	0			0

Research Reports

20 nm

Femtosecond-Resolved Polarimetry Probes of Electronic Nematicity in Iron Pnictides Magnetic Superconductors
Novel Project: Novel Characterization Tool

[2013-WAN-0113]
PI: Jigang Wang

Project Description

Understanding electronic *nematicity*, a unidirectional self-organized state that breaks rotational symmetry of the underlying lattice, has emerged as a cross-cutting theme critical for both high-temperature superconductivity and quantum magnetism. Studying nematicity has been essentially impossible from conventional static optical/electrical transport methods because they probe time-averaged properties, where the critical divergence of nematic fluctuations associated with developing new order are hidden inside. The goal is to reveal these dynamic fluctuations and disentangle correlation mechanisms in the time domain by using probing photo-excited femtosecond dynamics of the *nematic order* via ultrafast polarimetry. We will focus use the model superconductor systems Ba- and Ca-(Fe$_{1-x}$Co$_x$)$_2$As$_2$, and aim to establish this approach as a benchmark to other anisotropic interacting quantum fluids.

Mission Relevance

We directly target "*superconductivity*", "*ultrafast science*" and "*characterization of complex systems, emergent behavior*", identified from the DOE Basic Energy Science Grand Challenges and instrumentation needs. *Our research address non-equilibrium, mesoscopic quantum dynamics*, and aligns well with DOE new focus into the mesoscale sciences. Non-equilibrium quantum dynamics is one of the most pressing areas today in condensed matter physics, materials science, and device physics. This effort addresses materials for energy security mission.

FY2013 Results and Accomplishments

Our new capabilities and results thus far *provide a compelling pathway to advance non-equilibrium, mesoscopic quantum dynamics.* We developed new ultrafast instrumentation and applied it to study unstrained Ba(Fe$_{0.953}$Co$_{0.047}$)$_2$As$_2$ doped pnictides exhibiting antiferromagnetic and superconducting behavior. Our result provides a "*smoking gun*" for the critical divergence of nematic fluctuations [**Figure 1**], where *a **fast*** recovery occurs only in the magnetically
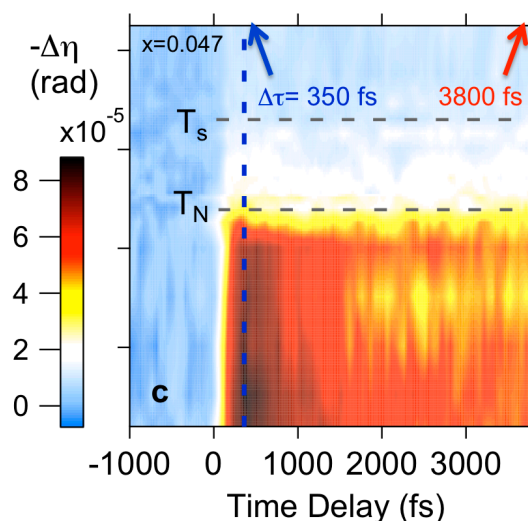

Figure 1. Femtosecond-resolved relaxation of Ising-nematic order parameter (i.e., in-plane anisotropy) after non-equilibrium photo-excitation at 1.55eV of unstrained Ba(Fe$_{0.953}$Co$_{0.047}$)$_2$As$_2$, showing a fast (slow) recovery below Néel T_N, (above T_N but below at T_S), with a strikingly sharp increase in relaxation time near T_S.

ordered state below the *Néel T_N*, and a ***slow*** recovery persists at higher temperature in a pure nematic phase between T_N and the structural transition at T_S, with increase in relaxation time.

FY2013 Additional Work Product

A. Patz, T. Li, S. Ran, R.M. Fernandes, J. Schmalian, S.L. Bud'ko, P.C. Canfield, I.E. Perakis, J. Wang, "*Ultrafast Observation of Critical Nematic Fluctuations and Giant Magnetoelastic Coupling in Iron Pnictides*," Nature Comm. **5**, 3229 (2014).

In addition, three major invitations to speak were received: *2014 Gordon Research Conference*: Ultrafast Phenomena in Cooperative Systems, *2013 Ultrafast Magnetism Conference, 2013 Int. Quantum Electronics Conference*.

FY2014 Proposed Work

Because we have demonstrated a powerful new benchmark approach that directly reveals critical nematic order parameter fluctuations in iron pnictides, we will study Ca- and Ba-based iron pnictides with different doping. The emphasis is to search for universal principles in quantum nematic matter, and to bridge the gap between elusive quantum physics and technologically relevant functionalities, e.g., colossal magnetoelastic coupling that far exceeds conventional magnetic metals.

Dynamic Whitelist Generation for Automated Intrusion Response
Novel Project: National (Cyber) Security

[2013-GOR-1218]
PI: Mark Gordon and Chris Strasburg

Project Description

As automation, sophistication, and potential damage of cyber attacks grow the Department of Energy and other organizations are under increasing pressure to automate cyber-defenses, e.g. blocking malicious websites. However, the risk of self-inflicted damage due to such automation is often significant. While *whitelists*, i.e., catalogs of resources that should not be disrupted, are one approach to mitigate this risk, manual construction of such lists is inherently error-prone and incomplete. Our goal is to develop an automated, learning-based approach to identify significant organizational relationships from network flow data, and then also examine its utility. These relationships can then be protected from disruption or identified for additional monitoring by automated cyber defense mechanisms.

Mission Relevance

For cyber-security mission, this project expects to directly demonstrate the utility of a *dynamic whitelist generation for automated intrusion response*. We will produce a packaged implementation suitable for sharing with other DOE sites – and the general public (an open-source utility). Automated identification of critical relationships between organizations will improve data confidentiality, integrity, and availability by enabling safe and effective use of automated cyber-defense, and focusing analysts' attention on those cyber events that have the highest expected mission impact.

FY2013 Results and Accomplishments

1. A prototype code was developed and ready for production testing within the Ames Laboratory cyber environment.

2. A feature set, labeling approach, and initial results have been generated experimentally.
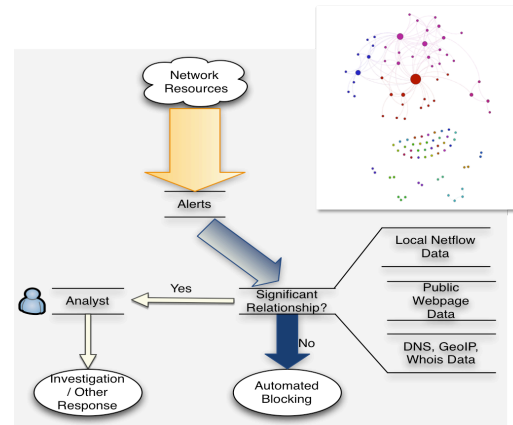

Figure 1. Dynamic whitelist model integrated into an analysts' workflow. Pop-out shows resource clusters produced by analyzing their public web sites and combining that data with network flow analysis.

FY2013 Additional Work Product

- Submitted technical paper to PNNL cyber-security publication. Received collaborative interest from cyber-security analysts Ashish Sharma (LBL) and Doug Nordwall (PNNL) in the Cooperative Protection Program.
- A poster was developed and submitted to the IEEE Super Computing (SC13) conference, and displayed at the at the DOE booth at SC13.
- In discussion with Tami Martin (ANL) about testing in their CARS (Cyber Automated Response System) program.
- Results presented at FloCON 2014, a network-flow based analysis conference, generating interest from industry (e.g., CISCO) and U.S. Government, US-CERT, suggesting collaboration to build a crowd-resource ID repository.
- Network Security Monitors presentation will be in May 2014 (postponed due to sequestration).

FY2014 Proposed Work

1. Complete production testing.
2. Recruit and assist pilot sites within DOE.
3. Assess the impact of this work for automated cyber defense at Ames and other DOE facilities.
4. Publish methods and results in key journal.
5. Pursue funding to develop models for additional cyber security threat data types.

Rapid, small-scale, high-purity rare-earth metal preparation
Strategic Initiative: MADDD

[2013-JON-0114]
PI: *Larry Jones and Trevor Riedemann*

Project Description

The project will develop a new methodology for small batch (≤500 gram) preparations of rare-earth metal (REM) having the required high purity for use in fundamental materials research and discovery. Sources of *off-the-shelf* supplies will be identified (ex. crucibles) with the intent to eliminate the need for custom fabrication and reduce labor Input. This development will shorten the processing arc while maintaining the high purity standard for which Ames Laboratory REM is internationally recognized.

Mission Relevance

To support research into functional materials for energy security, a successful REM process will enhance our strategic initiative on materials synthesis and processing by developing small-scale production methods and process efficiencies. A new process can be leveraged by DOE rare-earth sciences program across the complex, e.g., EERE's Critical Materials Institute, an energy innovation hub, and may evolve technology transfer. Our work *enhances* our process capabilities and *perpetuates* our position as *the* pre-eminent producer of the world's purest REMs for research. From this tested method, Ames Laboratory technical staff will be trained in these new capabilities, and, by extension, so will the REMs community.

FY2013 Results and Accomplishments

Several key steps were completed to date including repurposing of an under utilized crystal growth furnace for the rare earth reductions and vacuum casting processes. A new induction heater was designed, fabricated, and installed; temperature controls were added and any unnecessary crystal growth system components were removed.

Grandview Materials, Lewis Center, Ohio was identified as a supplier of "off-the-shelf" tantalum crucibles, and four crucibles were procurred. A cost reduction of 57% ($528.00) was realized over fabrication of crucibles in-house. Oxides and other necessary material inputs were obtained.

Figure 1. Reduction crucible with lid, TC well, and graphite insulation. Calcium fluoride slag (A) is removed (B) exposing the as-reduced REM (C).

Following initial induction heater testing, fluoride was prepared by fluorination processing, and the first metal preparation reduction was completed. Re-tuning of the heating system was required to achieve more uniform heating of the crucible and a second preparation reduction was completed.

FY2013 Additional Work Product

Fluoride Mass (g)	RE Metal Mass (g)	Yield (%)
250	184	99.4
450	331	99.3
TOTAL:	515	99.35

We **achieved >99.3%** yield for small-batch process.

FY2014 Proposed Work

Vacuum casting and distillation will complete the first preparation of the three proposed runs. Analysis of the completed metal will be and compared with historical quality REM. Vacuum system modifications may be required to achieve higher vacuum levels for final metal purification by distillation. Modifications to processing procedures will be evaluated and two more processing runs will be conducted and evaluated. Procedures based on successful completion will be drafted and transferred to Metals Processing Center (MPC) for use in future REM production, and potential technology transfer.

Demistifying Hydration Layer on Nano Oxide in Suspensions by Liquid Cell Transmission Electron Microscopy
Strategic Initiative: MADDD

[2013-AKI-0310]
PI: Mufit Akinc and Tanya Prozorov

Project Description

Using a *Continuous Fluid Flow Liquid Cell Platform* with the transmission electron microscope (TEM), we are attempting to study hydration of oxide nanoparticles in liquids. Our goal is to use *in-situ* liquid cell characterization of alumina *nano*-powder dispersions to demonstrate that this unique and powerful technique to ceramic nanoparticle suspensions can probe the hydration layer around these nanoparticles and monitor its thickness.

Mission Relevance

Rheological behavior of nanoparticle suspensions is of high importance in many existing sectors of industry, and any improvements to the inherent flow characteristics translates to large cumulative energy savings – part of our energy security mission. However, the control over these systems relies on a fundamental understanding of the underlying processes, including the hydration of suspended nanoparticles, as well as their stability, flocculation, and flow dynamics.

FY2013 Results and Accomplishments

In these proof-of-concept experiments, we demonstrated the formation of the hydration layer around the alumina nanoparticles. The TEM analysis of the dry alumina nanoparticles (**Figure 1 a)** points to spherical nanoparticles of various sizes, whereas the nanoparticles imaged in the liquid cell (**Figure 1 b),** reveal the presence of the hydration layer. It is worth noting that the technique provides enough contrast to differentiate between the particle, hydrated layer and the surrounding water. Interestingly, the HL appears to be 5-7 nm thick, which is in excellent agreement with the values calculated from the LT-DSC data.

We have established, that once formed, the hydration layer does not disappear upon drying particles at room temperature in air. We have also observed that particles tend to dissolve under radiation upon long-term exposure to electron beam. TEM images are captured in both the Bright Field and STEM modes. To compliment imaging
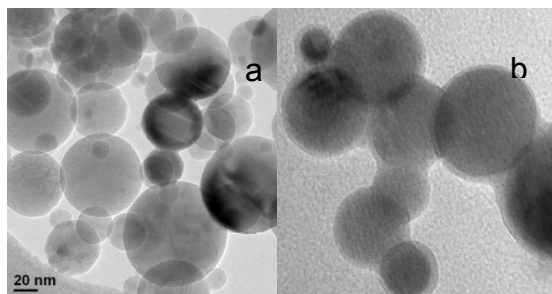

Figure 1. TEM images of a) dry Al_2O_3 particles, and b) in aqueous suspension, with notable formation of hydration layer around particles.

work, Electron Energy Loss Spectroscopy (EELS) data for oxygen and alumina are also acquired. EELS spectrum indicate that the signal appears to be due to the Al_2O_3 edge.

FY2014 Proposed Work

In FY2013 we have established, beyond a doubt, presence of the hydration layer via Liquid Cell TEM. In FY2014, we will develop the experimental protocols to observe the nanoparticles in a Liquid Cell in a continuous fluid flow mode. The optimization parameters will include cell alignment, solvent composition, nanopowder slurry loading, fluid flow, and acquisition modes.

Electron Energy Loss Spectroscopy and Energy-Filtered TEM are utilized to probe the localized chemical environment of the specimens and processes taking place on the surface of the nanometer-sized powder upon its exposure to the solvent. Relying on our previous rheology work, aqueous solutions will be studied with continuous flow liquid cell. Hydration layer will be probed as a function of various additives, solvent, time, and additive concentration to establish the growth kinetics of the HL and to investigate its thickness evolution. We will attempt to correlate Liquid Cell TEM findings with the results we have obtained from LT-DSC and rheology.

FY2013 Additional Work Product

A manuscript is in preparation for refereed journal.

In Situ, Real-Time Imaging of Single Site Catalysts in Turnover Conditions
Strategic Initiative: GrACE

[2013-FAN-0313]
PI: Ning Fang, Javier Vela; Wenyu Huang

Project Description

Real-time imaging of catalyst active sites *in situ* enables detailed study of fundamental reaction steps under actual turnover *operando* conditions. Using super resolution 3D imaging developed by us at Ames Lab, we study semiconductor-metal hybrid catalysts and silica-metal multilayer catalysts for *solar-to-chemical energy conversion and alcohol reforming*. Using our demonstrated ability to resolve single-molecule events with high resolution, we map and study *in situ* the reactivity (activity, selectivity, kinetics) of single catalytic active sites.

Mission Relevance

This research leverages our expertise to apply high-resolution and super localization techniques to study heterostructured catalysts for vertical (rather than incremental) improvements in chemistry and materials science to *develop functional materials for energy security*. Successes will transform our ability to predict the activity, selectivity and properties of new catalytic materials, which aligns with Ames Lab's initiatives (GrACE) and DOE Materials Genome initiatives, and Energy Security missions for the national lab complex.

FY2013 Results and Accomplishments

(1) High-resolution super localization imaging was employed to identify *two distinct mechanisms* of separation of photo-generated electrons in semiconductor-metal hybrid heterostructures. The mechanisms result in redox-active semiconductor-metal photocatalysts of completely opposite polarity (**Figure 1A**). Due to the different location of electrons (e-) and holes (h+), both of these charge-separated species is capable of performing different catalytic reactions with specific activity and selectivity.

(2) A highly modular multi-layer platform (**Figure 1B**) with controllable pore size, length, and active site location was used to detail activity, selectivity, and molecular transport in porous materials. Single-molecule turnover events were imaged by our one-of-a-kind 3D imaging
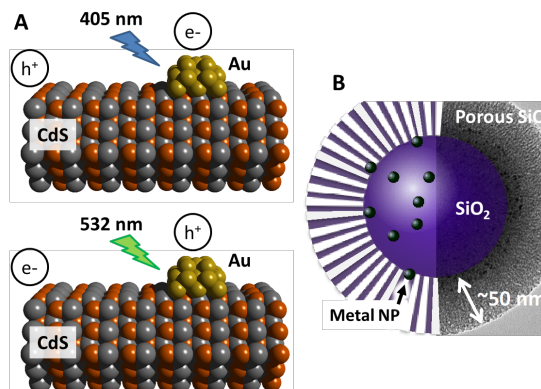

Figure 1. (A) Two distinct, incident energy-dependent charge separation mechanisms in Au-CdS hybrid heterostructures.
(B) The multi-layer core/nanoparticle/mesoporous oxide shell platform.

techniques with nanometer resolution in all three dimensions.

FY2013 Additional Work Product

J.W. Ha, T.P. Ruberu; R. Han; B. Dong; J. Vela; N. Fang, "*Super-resolution Mapping of Photo-generated Electron and Hole Separation in Single Metal-Semiconductor Nanocatalysts*," J. Am. Chem. Soc. 136, 1398-1408 (2014)

FY2014 Proposed Work

Using high-resolution, super localization imaging techniques, we will study the interactions between single fluorescent molecules and the surface active sites on single metal-semiconductor nanocatalysts and map 3D reactivity patterns on multi-layer core/metal nanoparticle/mesoporous oxide shell nanocatalysts. We will acquire a deeper understanding of the nature of surface active sites, the photocatalysis mechanisms operating on the metal-semiconductor heterostructures, and the interaction between single molecules and surface active sites, as well as the plasmon-induced hot electrons that are recently gaining much attention in photochemistry. The knowledge gained from the fundamental studies will further enable us to address a grand challenge for photocatalysis in understanding the connections between the catalyst structure and catalytic activity and selectivity. This will then enable the design of efficient nanocatalysts for energy-relevant applications, such as the photocatalytic reduction of CO_2 to hydrocarbon fuels under visible light at room temperature.

Atomic and Electronic Level Control of Nanocluster Catalysts Encapsulated in Metal-Organic Frameworks (MOFs)
Strategic Initiative: GrACE

[2013-HUA-0413]
PI: Wenyu Huang and Linlin Wang

Project Description

This initiative aims to <u>control</u> heterogeneous catalytic properties of nanoclusters (NCs), and to <u>connect</u> those properties to the atomic and electronic features around the NCs. Controlling heterogeneous catalysis at the atomic and electronic level represents one of the key scientific challenges for technology. Using MOFs as hosts of metal NCs, we could reach an atomic- and electronic-level control of heterogeneous catalysts due to the well-defined structure of MOFs.

Mission Relevance

DOE-BES has identified (reports: "Catalysis for Energy" and "Directing Matter and Energy: Five Challenges …") catalytic technology as essential for sustained economic development, energy security, and environmental preservation for our society. To synthesize high-performance catalysts, and design materials with desired catalytic properties, we need to improve our understanding of the structure – catalytic property relationship at the atomic and electronic level, exactly our research objectives.

FY2013 Results and Accomplishments

We discovered one key to making uniform platinum NCs in a Zr-MOF – site and symmetry of platinum (Pt) ions in the MOF having cis- or trans- orientation when binding to NH_2 ions. This discovery will help to understand many other important applications of MOFs based on host-guest interactions, such as gas storage, chemical adsorption and separations, catalysis, sensors, and drug delivery.

Only by integrating experiments with theory and simulations was this discovery possible. We used Extended X-ray Absorption Fine Structure (EXAFS) experiments to extract coordination environments of Pt-ions in the MOF. EXAFS data was collected at the *Advanced Photon Source* at Argonne National Laboratory. Only by matching atom coordination data from theory and experiment did a coherent picture emerge.
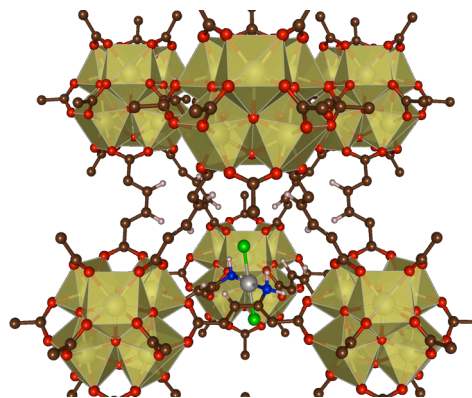

Figure 1. Most stable configuration of $PtCl_2$ bonded to two NH_2 groups in a functionalized Zr-MOF. Brown (white) spheres are C (H). Yellow (red) are Zr (O). Blue, grey and green are N, Pt and Cl.

From EXAFS, Pt coordination is 2.6-2.2 nitrogen atoms with a bond length of 2.06-2.07 Å, and 1.3-1.7 chlorine atoms with a bond length of 2.30-2.31 Å. The total coordination number surrounding Pt atom was 3.9-4.1, consistent with Pt(II) ion surrounded by four coordinated ligands.

The atomic number of N is close to that of O, so EXAFS cannot tell if it is N or O surrounding a Pt. Collaborating with NMR specialists at the Ames Laboratory, we used ^{13}N NMR and confirmed the coordination of N with Pt ions, and that the N is from the amine groups on the MOF.

Density functional theory calculations provide a clear picture of the binding sites in the MOF and the specific geometry of the Pt ions. The most stable configuration is planar for $PtCl_2$-$2NH_2$, which sits on a triangular facet in Zr-MOF (**Figure 1**). Average Pt-N (Pt-Cl) bond length of 2.14 (2.33) Å agrees well with our EXAFS results.
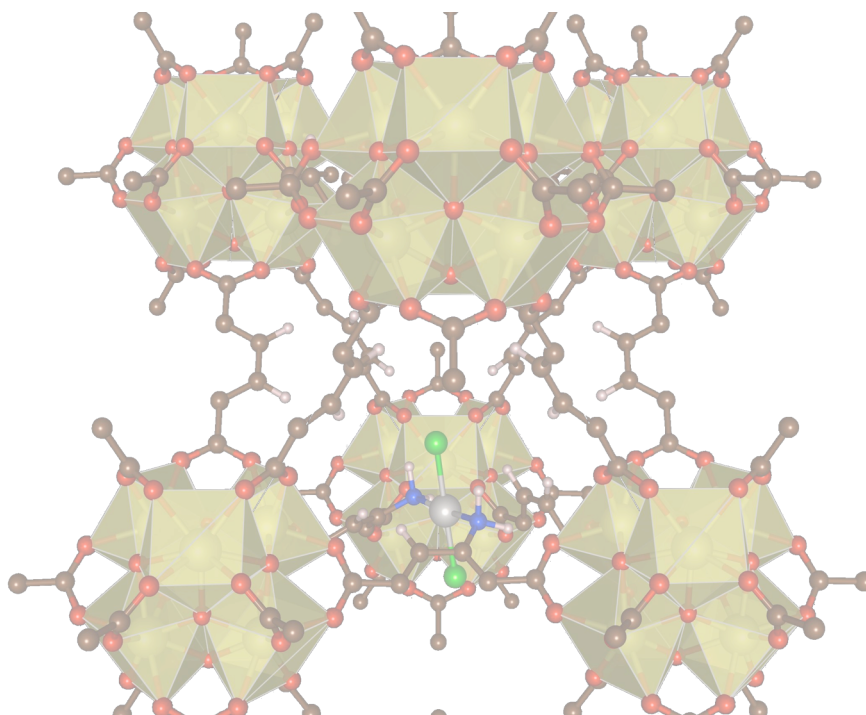
FY2013 Additional Work Product

Manuscript was submitted to high-impact journal.

FY2014 Proposed Work

Now knowing how to create uniform Pt NCs in the MOF, we will study the selectivity of the catalysts using MOFs with similar structure but different functional groups for the catalyst support. Using *ab initio* molecular dynamics, we will explore more of the adsorption configurational space in the MOFs and elucidate the origin of selectivity in NC/MOF catalysts for a designer catalyst for industry.

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U.S. DEPARTMENT OF ENERGY